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Title: Abradability aluminum oxide ceramics and its manufacture method

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Abstract

A aluminum ceramics capable of sintering at a low temperature, free from unevenness in characteristics and excellent in wear resistance with low-cost starting materials. 88 to 95 wt.% of Al2O3 is used as the principal component of aluminum ceramics and 3.6 to 10 wt.% SiO2, 0.2 to 2.5 wt.% MgO and 0.2 to 2.5 wt.% CaO are added by 5 to 12 wt.%, in total, as subsidiary components to the alumina. When the total amount of the SiO2, MgO and CaO is represented by 100 wt.%, the amounts of the SiO2, MgO and CaO are 72 to 85 wt.%, 3 to 25 wt.% and 3 to 25 wt.%, respectively. The amount of inevitable impurities is reduced to less than 0.5 wt.%, the amount of defects is limited to less than 5%.

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2-1 Claims

1. A wear-resistant alumina ceramics, characterized in that said alumina ceramics is
5 consisted of 88% (weight) or more and 95% (weight) or less of Al₂O₃, 5-12% (weight) of auxiliary components and 0.5% (weight) or less of impurities; said auxiliary components being consisted of 72-85% (weight) of SiO₂, 3-25% (weight) of MgO, and 3-25% (weight)
10 of CaO; the weight percentages occupied by each component in said auxiliary components relative to said ceramics as a whole being the following: SiO₂ 3.6-10% (weight), MgO 0.2-2.5% (weight), CaO 0.2-2.5% (weight), respectively, and the defect ratio of said ceramics being 5% or less.
2. The wear-resistant alumina ceramics according to claim 1, characterized in that, relative to per 100 weight parts of basic composition consisted of 88% (weight) or more and
15 95% (weight) or less of Al₂O₃, 3.6-10% (weight) of SiO₂, 0.2-2.5% (weight) of MgO, 0.2-2.5% (weight) of MgO and the remainder of impurities, 0.01-15 weight parts of ZrO₂ is added.
3. The wear-resistant alumina ceramics according to claim 1, characterized in that as
20 the impurities described above, alkali metal oxides has a content of 0.4% (weight) or less, and TiO₂ has a content of 0.2% (weight) or less.
4. The wear-resistant alumina ceramics according to any one of claim 1-3, characterized in that said alumina ceramics has an average crystal particle diameter of
25 1.0-5.0 μm and a volume density of 3.60 g/cm³ or more.
5. A method for manufacturing the alumina ceramics according to claim 1, characterized in that, formulating the feed powders with a predetermined ratio, micropulverizing this mixture into the powders with an average particle diameter of 0.5-1.0
30 μm , and then shaping the micropowders obtained into a desired shape to obtain a shaped

article with an volume density of 1.90-2.10 g/cm³, and baking the shaped article.

2-2 (Page 2, lines 9 to 15 of the Specification):**Means of solving the problem**

The means of the present invention for attaining the object described above is to provide a wear-resistant alumina ceramics, being consisted of 88% (weight) or more and 5 95% (weight) or less of Al_2O_3 , 5-12% (weight) of auxiliary components and 0.5% (weight) or less of impurities; said auxiliary components being consisted of 72-85% (weight) of SiO_2 , 3-25% (weight) of MgO , 3-25% (weight) of CaO ; the weight percentages occupied by each component in said auxiliary components to said ceramics as a whole being the following: SiO_2 3.6-10% (weight), MgO 0.2-2.5% (weight), CaO 0.2-2.5% (weight) respectively, the 10 defect ratio of said ceramics being 5% or less.

2-3 (Page 3, line 3 to page 4, line 34 of the Specification):

That is, the wear-resistant alumina ceramics of the invention is characterized in that: said alumina ceramics is consisted of 88% (weight) or more and 95% (weight) or less of 15 Al_2O_3 , 3.6-10% (weight) of SiO_2 , 0.2-2.5% (weight) of MgO , 0.2-2.5% (weight) of CaO , and the remainder being substantively the inevitable impurities; the sum of the contents of SiO_2 , MgO and CaO described above is 5-12% (weight); provided that the sum of contents 20 of SiO_2 , MgO and CaO described above is 100, the proportions of each of the components are the following: SiO_2 72-85% (weight), MgO 3-25% (weight), CaO 3-25% (weight), respectively, the content of the inevitable impurities is 0.5% (weight) or less, and the defect ratio is 5% or less.

The content of Al_2O_3 which is the main component described above is more preferable to be in the range of 90-94.5% (weight). Furthermore, the contents of the auxiliary components described above are preferable to be the following: SiO_2 5-10% (weight), MgO 25 0.4-1.5% (weight), CaO 0.3-1.5% (weight); when the sum of each of the components described above is provided to be 100, it is more preferable that the proportions of each component are in the range of SiO_2 73-84% (weight), MgO 3.5-1% (weight), and CaO 4-15% (weight).

Additionally, in the invention, in order to further increase the strength and toughness of 30 the alumina ceramics described above, and at the same time, to make the microscopic

structure thereof being more uniform, 0.01-15 weight parts, preferably 0.05-10 weight parts, more preferably 0.1-8 weight parts of ZrO₂ are add into each 100 weight parts of a basic composition consisted of the aforementioned components.

Additionally, the invention provides a method of manufacturing the wear-resistant alumina ceramics, characterized in that: formulating the feed powders with predetermined ratio, micropulverizing this mixture into the powders with an average particle diameter of 0.5-1.0 μm, and then shaping (molding) the micropowders obtained into a desired shape to obtain a shaped article, and baking this shaped article. Here, the specific surface area of the pulverized micropowders is preferably 8-15 m²/g, and the temperature of baking the shaped article is preferably 1350-1600°C.

The content of the aforementioned inevitable impurities is set to be 0.5% (weight) or less, however, among others, it is preferable to set the content of alkali metal oxides such as Na₂O and K₂O and the like to be 0.45% (weight) or less, more preferably 0.4% (weight) or less. Furthermore, the content of TiO₂ is set to be 0.2% (weight) or less, more preferably 0.15% (weight) or less.

Additionally, the each of the components described above has great affect on the wear-resistant property of the ceramics. Thus, it is preferable to control the defect ratio on the mirror polishing face to be 5% or less. The reason lies in that if the defect ratio exceeds 5%, these defects will become the starting points of abrasion, accelerating the abrasion, thus resulting in the drop of the wear-resistant property, simultaneously, resulting in the inferiority of the impact resistant strength, so it is undesirable. The defect ratio is preferably 3% or less, more preferably 2% or less.

Mode for carrying out the invention

As described above, the wear-resistant alumina ceramics of the invention is prepared by: formulating the feeds according to the ratio as described above and pulverizing this mixture into the powders with an average particle diameter of 1.0 μm or less and specific surface area of 8 m²/g or more, more specifically, formulating the feed powders with the average particle diameter of 0.5-1.0 μm and the specific surface area of 8-15 m²/g, sinter-shaping the feed powders obtained into a predetermined shape to obtain a shaped

article with a volume density of 1.90-2.10 g/cm³, and then baking this shaped article at a temperature of 1350-1600°C. The specific manufacture method is as follows.

(1) Firstly, formulating the compounds of each compositional element constituting the alumina ceramics according to the component ratio described above, and adding ZrO₂ feeds if necessary, then performing pulverization, mixing, dispersion by wet method using the known pulverizers such as ball milling machine, roll milling machine and the like in water or an organic solvents to formulate the feed powders.

As the main component, the alumina feed has a purity of 99.7% (weight), a specific surface area of 2 m²/g or more and an average particle diameter of 3.0 μm or less, more preferably an average particle diameter of 0.5-3.0 μm. Furthermore, the alumina feed can be made by Alum method; however, the most preferable alumina feed is made by using Bayer method, wherein the feed can be made inexpensively.

As the feeds of MgO and CaO in auxiliary components, the salts of oxides, hydroxides, carbonates and the like can be employed, but it is preferable to use the salts with an average particle diameter of 3.0 μm or less, more preferably with an average particle diameter of 0.5-3.0 μm. Furthermore, as SiO₂ feed, silica, quartz, silica sol, tetraethyl silicate and the like can be used, and what can be used also is quadratic system zirconium obtained by solid-dissolving the rare earth type elements of Y₂O₃ and the like as stabilizer into clay minerals such as kaolin and the like or CrO₂. As the feed of this ZrO₂, the feed with an average particle diameter of 1.0 μm or less, preferably an average particle diameter of 0.5-1.0 μm, and a specific surface area of 5 m²/g or more, preferably 5-16 m²/g or more is used. When using the quadratic system zirconium in which the stabilizers of Y₂O₃ and the like is solid-dissolved as the feed, the toughness thereof can be increased by the effect of stress-induced phase change.

In the feeds of alumina ceramics described above, inevitable impurities such as Fe₂O₃, Na₂O, K₂O and TiO₂ and the like are generally contained, however, since the alkali metal oxides and TiO₂ in the inevitable impurities either form secondary phase or result in the formation of abnormal particles, feeds in which the inevitable impurities are as few as possible should be used; in particular, since Na₂O and K₂O are easy to form glass phase with SiO₂ and the like, feeds in which the content of the alkali metal oxides is below 0.45%

(weight) should be used; furthermore, since TiO_2 either accelerates the growth of the crystals or becomes the reason of abnormal crystal grain growth, it should choose the feeds in which TiO_2 content is 0.2% (weight) or less, preferably 0.15% (weight) or less.

Pulverization, mixing and dispersion are preformed in water or organic solvents by wet method. Here, the viscosity of the slurry is preferable to be 50-1500 cps. When the viscosity is high, a dispersant such as sodium acrylate, polycarboxylate and the like is preferably added properly to adjust the viscosity. The powders obtained by pulverization have an average particle diameter of 1.0 μm or less and a specific surface area of 5 m^2/g or more, more specifically, the powders are pulverized into those having an average particle diameter of 0.5-1.0 μm and a specific surface area of 8-15 m^2/g or more. In order to perform the pulverization with such particle size, for example, a ball milling machine can be used to carry out the pulverization for 96 h using milling balls made of alumina with the diameter of 20 mm.

(2) drying and granulating the slurry obtained as above to obtain granulated powders. The drying methods can be selected according to the forming methods used, and generally, when forming by using molding or CIP (isotropic rolling) methods, spray drying is employed; and in the case of casting forming and rotating granulation forming or in the case of using extrusion forming and injection forming, drying with a desiccator is preferably be selected.

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2-4 (Page 5, line 27 to page 14, line 13 of the Specification):

The shaped article obtained as above is baked at a temperature of 1350-1600°C, preferably 1400-1550°C, such that the object product of wear-resistant alumina ceramics is obtained.

25 The reasons for which the components of the wear-resistant alumina ceramics related to the invention are limited to the range as described above are as follows. That is, the content of Al_2O_3 should be 88% (weight) or more and 95% (weight) or less. If the content of Al_2O_3 is less than 88% (weight), the amounts of glass phase and secondary phase formed in the inside of the sintered body will be increased which cause the strength and hardness of 30 the sintered body inferior, and the impact resistant property and wear-resistant property

thereof are also dropped, thus it is undesirable. Furthermore, if the content of Al_2O_3 is above 95% (weight), not only glass phase formed in the inside of the sintered body will be too less which causes the sintering property inferior, but also as the baking temperature is increased, the segregation of glass phase will be likely to be produced on the grain boundary of 5 alumina, which becomes the reason of abnormal crystal grain growth and makes the hardness, toughness and strength inferior, thus it is also undesirable.

Furthermore, SiO_2 , MgO and CaO as the auxiliary components described above are added as sintering aids, and these auxiliary components are present mainly as glass phase on the grain boundary of alumina, which restrains the growth of crystal grains thereof, 10 increases the volume density, restrains the defect ratio inside and increases the wear-resistant property. Limiting the contents of each auxiliary component to the range described above is based on the reasons as described below.

That is, when the contents of SiO_2 , MgO and CaO are in the range of SiO_2 3.6-10% (weight), MgO 0.2-2.5% (weight), CaO 0.2-2.5% (weight), respectively, not only the 15 thermal expansion differential and wetting property between them and Al_2O_3 crystals are adequate and the crystal particle diameter and distribution are controllable easily, but also the strength and the toughness of the grain boundary of alumina are increased, thus the impact resistant property and the wear-resistant property are increased. However, when the content of any one of SiO_2 , MgO and CaO exceeds the ranges described above, in addition. 20 to the drop of the strength of grain boundary of alumina, the formation of secondary phase particles, the abscission of the crystal particle diameter due to the impact and friction with other materials and the inferiority of toughness, the crystals become larger at the baking stage and the (over)growth of abnormal crystal grains occurs easily, which results certainly in the absence of uniformity for crystal particle diameter so that the impact resistant 25 property and the wear-resistant property drop, so the ranges described above are selected.

Specifically, when the content of SiO_2 is less than 3.6% (weight), the sintering property of the alumina ceramics is inferior. Furthermore, when the content of SiO_2 exceeds 10% (weight), it will result in the grain boundary intensity of alumina ceramics inferior, so the values described above are selected. Additionally, when the content of MgO is less than 30 0.2% (weight), the crystal particle diameter of the alumina ceramics is short of uniformity;

and when the content of MgO exceeds 2.5% (weight), the secondary phase will be precipitated, therefore the content of 0.2-2.5 % (weight) for MgO is selected. Furthermore, when the content of CaO is less than 0.2% (weight), the sintering property of the alumina ceramics is inferior; and when the content thereof exceeds 2.5% (weight), it will also result
5 in the sintering property of alumina ceramics inferior and the growth of abnormal grains, so the content of 0.2-2.5% (weight) for CaO is selected.

In addition, the sum of the contents for SiO₂, MgO and CaO, that is, the content of auxiliary components is selected as 5-12% (weight), the reason lies in: when the sum of the contents for the components described above is less than 5% (weight), the reduction in the
10 amount of the glass phase existing at the alumina grain boundary makes the presence of glass phase being non-uniform, which produces the drop of sintering property and the growth of abnormal crystal grains of the crystals, thereby resulting in the impact resistant property and wear-resistant property of alumina ceramics inferior. Therefore, it is unsuitable to use. On the other hand, when the content of auxiliary components exceeds 12% (weight),
15 the glass phase is formed too much, which results in the hardness, toughness and strength of alumina ceramics inferior, thereby reducing the impact resistant property and wear-resistant property of alumina ceramics, so the aforementioned range is selected.

Furthermore, provided that the sum of the contents for SiO₂, MgO and CaO described above is 100, the reason that the proportions of each of the components are SiO₂ 72-85%,
20 MgO 3-25% (weight), CaO 3-25% (weight) respectively is as follows. That is, when the content of SiO₂ in the auxiliary components is less than 72% (weight), the sintering property of alumina ceramics is inferior. Furthermore, the amount of the glass phase increases when the content of SiO₂ in the auxiliary components exceeds 85% (weight). So the aforementioned range is selected. In addition, when the content of MgO is less than
25 3% (weight), the crystal particle diameter of the alumina ceramics is short of uniformity; and when the content of MgO exceeds 25% (weight), secondary phase will be precipitated; therefore the range described above is selected as the content of MgO in the auxiliary components. Furthermore, when the content of CaO in the auxiliary components is less than 3% (weight), the sintering property of the alumina ceramics is inferior; and when its content
30 exceeds 25% (weight), it will not only result in the sintering property of alumina ceramics

inferior, but also make the crystals growing easily, so the aforementioned range is selected as the content thereof.

Relative to 100 weight parts of a basic composition consisted of the aforementioned components, 0.01-15 weight parts of ZrO_2 are added into the wear-resistant alumina 5 ceramics of the invention, thereby further increasing the strength and toughness, and at the same time, making the glass phase in grain boundary of alumina dispersed in a uniform manner. Furthermore, it can also decrease the distribution of crystal particle diameter and make the structure of the sintered body uniform. The reason for setting the aforementioned range for the addition amount of ZrO_2 lies in: when the addition amount thereof is less than 10 0.01 weight parts relative to per 100 weight parts of the basic composition consisted of the aforementioned components, a sufficient effect cannot be achieved; and when this addition amount exceeds 15 weight parts, it will in turn result in an inferior hardness. Particularly, when using ZrO_2 powders without the addition of a stabilizer, monoclinic zirconium tends to be existed in the sintered body which may produce microcracking, thereby making the 15 wear-resistant property and impact resistant property thereof inferior, so it is undesirable. Relative to per 100 weight parts of the basic components described above, the aforementioned addition amount of ZrO_2 is 0.01-15 weight parts, preferably 0.05-10 weight parts, and more preferably 0.1-8 weight parts.

Here, the ZrO_2 feed added preferably is a feed with an average particle diameter of 1.0 20 μm or less. The reason lies in that when the average particle diameter of ZrO_2 feed exceeds 1.0 μm ; monoclinic system zirconium tends to be existed in the sintered body which may produce microcracking, thereby making the wear-resistant property and impact resistant property thereof inferior. Thus, it is undesirable. Furthermore, as the ZrO_2 feed, the feeds solid-dissolved with the stabilizers of rare earth type element oxides or the like can also be 25 used. Here, for the ZrO_2 feed containing rare earth type elements oxides, such as Y_2O_3 , as stabilizer, the feed with Y_2O_3 content of 5% (mole) or less is preferably used; thereby the toughness can be increased by the effect of stress-induced phase change of zirconium.

As described above, according to the invention, specific amounts of specific auxiliary components are added in a predetermined ratio into the Al_2O_3 being main component, while 30 restraining the amount of the inevitable impurities contained in the feed, thereby the alumina

ceramics with excellent wear-resistant property can be obtained, wherein the alumina ceramics described above have an average crystal particle diameter in the range of 1.0-5.0 μm and a volume density of 3.60 g/cm^3 or more, additionally, and the defects of particle ablation or the like caused by pores and polishing treatment is less, being 5% or less.

5 In addition, when the average crystal particle diameter of the sintered body exceeds 5 μm , it will result in the hardness and decreased wear-resistant property of the alumina ceramics inferior, so it is undesirable. The average crystal particle diameter of the sintered body is preferably 3 μm or less, more preferably 2.5 μm or less, additionally, in the case where the chipping-resistant property is not a problem, in view of the balance between it and
10 the wear-resistant property, it is preferable to set the average crystal particle diameter in the range of 5 μm or less. Furthermore, when the largest particle diameter thereof (the crystal particle diameter when the cumulative volume is 100%) exceeds 10 μm , the distribution of crystal particle diameter becomes wider and the hardness is inferior. This result is related to the inferiority of the wear-resistant property and is unsuitable for use, thus it is preferable to
15 use the sintered body with the largest particle diameter of 10 μm or less, and more preferably 8 μm or less.

Additionally, the volume density is selected as 3.60 g/cm^3 or more, the reason lies in that when the volume density is less than 3.60 g/cm^3 , the degree of sintering is not enough, and at the same time, there is many pores to be defects, which not only causes the inferiority
20 of the strength, hardness and toughness, but also accelerates the abrasion, thus it is undesirable. It is preferable to select the volume density of 3.65 g/cm^3 or more.

The alumina ceramics of the invention has excellent impact resistant property and wear-resistant property because of small crystal particle diameter, dense crystals and less defects. Therefore, comparing with the conventional sintered body with the same level of
25 Al_2O_3 content, the alumina ceramics of the invention has high strength, large hardness and good toughness. The Vickers hardness of the alumina ceramics of the invention shows high hardness of 1100 or more under the load of 10 kgf. Additionally, the bending strength thereof shows high strength of 40 kgf/mm^2 or more under 3 points bending method specified by JIS1610. Furthermore, when the alumina ceramics of the invention is made into such a
30 ball shape as milling balls for pulverization, a milling ball body is embedded into a super

hard alloy plate and a stress is applied, the compression strength measured is 25 kgf/mm² or more. This compression strength (σ_c) can be obtained from the formula: $\sigma_c = 4 \times P / (\pi \times D^2)$ (kgf/mm²). In the formula, P is breaking strength; and D is the diameter of the ball (mm).

5 The wear-resistant property drops when the Vickers hardness is less than 1100. So it is undesirable. Additionally when the bending strength is less than 40 kgf/mm² or the compression strength is less than 25 kgf/mm², it will affect and reduce the impact resistant property and the wear-resistant property, and thus it is undesirable, either. Furthermore, the breaking toughness in the measurement method specified by JIS1617 (IF method) is 3.0
10 MPa $\sqrt{\text{m}}$ or more.

Example 1

A sintered body is obtained by blending each feed according to the compositions of Table 1, and Table 2. each mixture was wet pulverized under the concentration of 60% for 15 48 h by using a ball milling machine made of 92% alumina (capacity: 7.2 cubic liter) and milling balls made of 92% alumina with the diameter of 20 mm, to obtain a slurry containing the fine powders having average particle diameters as showed in Table 3, Table 4 and specific surface area of 8 m²/g or more. To the slurry obtained, a 3-5% (weight) of aqueous polyvinyl alcohol solution as a adhesive was added to adjust the viscosity to be 350
20 cps, and dried by using a spray dryer sustained at 200°C, and granulated to obtain the powders for forming. Under a forming pressure of 1 ton f/cm² (in the case of Sample No. 20 and No. 38, the forming pressure was 300 kgf/cm²), the powders for forming were formed into ball shape and plate shape by CIP forming method. The shaped article was baked at 1380-1600°C to obtain a ball having a diameter of 10 mm and a 50 × 50 × 4 mm plate. The
25 ball, after barrel polishing, was used as the ball for pulverization; and the plate, after cutting and grind-cutting treatment, was used as the test sheet for the bending strength test specified by JIS1601.

As alumina material, as to Sample Nos. 1-21, 24-39, the agglomerated low-sodium alumina feed with a secondary particle diameter of 45 μm , a specific surface area of 2.5
30 m²/g and a purity of 99.6% made according to Bayer method was used respectively; as to

Sample No. 22, the active alumina feed with an average particle diameter of 1.0 μm , a specific surface area of 6 m^2/g and a purity of 99.8% was used; and as to Sample No. 23, the agglomerated low-sodium alumina feed with a secondary particle diameter of 55 μm , a specific surface area of 1.5 m^2/g and a purity of 99.7% made according to Bayer method was
5 used.

Additionally, as the feeds of MgO and CaO, carbonates with a purity of 99.5% were used; and as the feed of SiO₂, kaolin was used. As the feed of ZrO₂, in Sample Nos. 5, 8, 10, 15 and 25, zirconium dioxide with an average particle diameter of 1.0 μm , a specific surface area of 12 m^2/g and a purity of 99.9% was used; and in Sample No. 13, zirconium dioxide containing Y₂O₃ 2.8% (mole) and having an average particle diameter of 0.5 μm and a specific surface area of 18 m^2/g was used.
10

Wear-resistant test was performed according to the method as described below using each ball for pulverization obtained. That is, the balls for pulverization were loaded into a ball milling machine with a volume of 2 L made of alumina (purity: 92%) to one half
15 volume of the ball milling machine, and 900 g of alumina feed powders with an average particle diameter of 25 μm , and a specific surface area of 1.2 m^2/g and 0.7 L of water were added, and then pulverization was carried out in the ball milling machine under the rotation speed of 100 rpm for 24 h. The percentage relative to the weight of the ball before measurement was calculated from the weight differential of the ball before and after the
20 measurement and was regarded as abrasion ratio. The results obtained and the volume density of the ball for pulverization, crystal particle diameter, defect ratio, Vickers hardness, bending strength, the volume density of the shaped article, the average particle diameter and specific surface area of powders for pulverization were shown together in Table 3, and Table 4. The bending strength was measured by a test sheet processed from the plate.

Table 1

Sample No.	main component Al ₂ O ₃ (weight %)	basic composition						ZrO_2 addition amount (weight part)	
		secondary component			impurities (weight %)				
		<u>secondary component (weight %)</u>		<u>the composition of the secondary component</u>					
		SiO ₂	MgO	CaO	SiO ₂	MgO	CaO		
	(weight %)	(weight %)	(weight %)	(weight %)	(weight %)	(weight %)	(weight %)		

Table 2 (Table 1 continued)

Table 3

Sample No.	average particle diameter (μm)	volume density of the shaped article	baking temperature (°C)	volume density (g/cm ³)	crystal particle diameter (μm)	maximum value	defect ratio (%)	HV	bending strength (kgF/mm ²)	abrasion ratio (%)

Table 4 (Table 3 continued)

In Table 1, and Table 2, the addition amount of ZrO_2 was shown relative to the addition amount (weight part) of 100 weight parts of the basic composition consisted of alumina, the sintering aids and the inevitable impurities. Furthermore, in Table 1, Table 2, Table 3 and Table 4, the sintered body of Sample Nos. 1-17 satisfied the conditions of the invention, but Sample Nos. 18-39 were the sintered body being not satisfied at least one of the conditions specified by the invention and fallen out of the range of the invention.

The average crystal particle diameter was obtained as follows: after abrasive machining the sintering body on a diamond grinding wheel in the order of No. 140-No. 400-No. 600, and further grinding on a diamond grinding wheel in the order of 40 μm -6 μm -3 μm -1 μm to be polished into mirror surface. To this, thermal etching was performed further, followed by an observation on a scanning electron microscope with a magnification that more than 100 crystals can be observed in a view field, and a photograph was taken. The area of a crystal was measured from this photograph by picture analysis and converted into equivalent circle diameter (D), and the crystal particle diameters of 100 crystals were measured in this way by taking $D \times 1.5$ as the crystal particle diameter. The volume of the crystal was calculated according to these values, and the crystal particle diameter, when the cumulative volume is 50%, was taken as the average crystal particle diameter.

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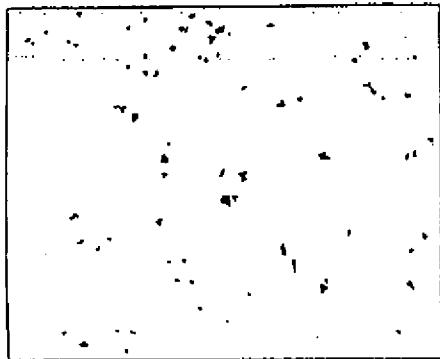
[74] 专利代理机构 上海专利商标事务所
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[54] 发明名称 耐磨性氧化铝陶瓷及其制造方法

[57] 摘要

一种低成本的具有优异耐磨性能的氧化铝陶瓷，所述的氧化铝陶瓷可在低温下烧结，且特性不匀小。本发明以 Al₂O₃ 88 - 95% (重量) 为氧化铝陶瓷的主要成分，再添加由 SiO₂ 72 - 85% (重量)、MgO 25% (重量)、CaO 25% (重量) 组成的辅助成分，使其中的各成分在氧化铝陶瓷的总量中所占的量为 SiO₂ 3.6 - 10% (重量)、MgO 0.2 - 2.5% (重量)、CaO 0.2 - 2.5% (重量)，上述成分的总量占氧化铝陶瓷的总量为 5 - 12% (重量)；同时，将不可避免的杂质含量控制在 0.5% (重量) 以下，另外，陶瓷缺陷率控制在 5% 以下。



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权 利 要 求 书

5 1. 一种耐磨性氧化铝陶瓷，其特征在于，所述的氧化铝陶瓷由 Al_2O_3 88% (重量) 以上，95% (重量) 以下、辅助成分 5—12% (重量) 及杂质 0.5% (重量) 以下组成；所述辅助成分由 SiO_2 72—85% (重量)、 MgO 3—25% (重量)、 CaO 3—25% (重量) 组成；所述辅助成分中的各个成分对所述陶瓷整体所占重量百分比分别为 SiO_2 3.6—10% (重量)； MgO 0.2—2.5% (重量)， CaO 0.2—2.5% (重量)，所述陶瓷缺陷率在 5% 以下。

10 2. 如权利要求 1 所述的耐磨性氧化铝陶瓷，其特征在于，对于每 100 重量份由 Al_2O_3 88% (重量) 以上，95% (重量) 以下、 SiO_2 3.6—10% (重量)、 MgO 0.2—2.5% (重量)、 CaO 0.2—2.5% (重量) 及其余的杂质组成的基本组分物，添加 ZrO_2 0.01—15 重量份。

15 3. 如权利要求 1 所述的耐磨性氧化铝陶瓷，其特征在于，作为上述杂质的碱金属氧化物的含量为 0.4% (重量) 以下， TiO_2 在 0.2% (重量) 以下。

4. 如权利要求 1—3 之任一项所述的耐磨性氧化铝陶瓷，其特征在于，所述的氧化铝陶瓷的平均结晶粒径为 1.0—5.0 μm ，体积密度为 3.60 g/cm^3 以上。

20 5. 一种如权利要求 1 所述的氧化铝陶瓷的制造方法，其特征在于，以所定的比例配合原料粉末，将该混合物作微粉碎至平均粒径为 0.5—1.0 μm 的粉末后，将所得的微粉末定形成所需的形状，得到体积密度为 1.90—2.10 g/cm^3 的成型体，焙烧该成型体。

说 明 书

耐磨性氧化铝陶瓷及其制造方法

5 技术领域

本发明涉及一种耐磨性氧化铝陶瓷，特别是，本发明涉及一种可用于耐磨性部件材料的耐磨性氧化铝陶瓷及其制造方法。

已有技术

10 近年来，人们已经注意到陶瓷的耐磨性及耐腐蚀性能比金属材料优异，陶瓷材料正在取代已有的金属被用作为耐磨性部件材料。作为这种陶瓷，通常已知有氧化铝、氧化锆、氮化硅、碳化硅等。其中，以硬度大、具有优异的耐腐蚀性且价廉的氧化铝为主体的氧化铝陶瓷被广泛使用着。一般来说，氧化铝陶瓷如仅由氧化铝单体构成，则其烧结性能差，生产性差，因此，一般须添加如
15 烧结助剂或其它添加剂后进行焙烧。

发明欲解决的课题

然而，以往的氧化铝陶瓷存在的问题是：由于添加了大量的添加剂，氧化铝陶瓷中 Al_2O_3 的含量达 90 - 95 % (重量)，由此在氧化铝晶界上生成大量的除氧化铝结晶以外的次生相及玻璃相，得不到氧化铝本来的硬度及强度，且得不到充分的耐磨性。

20 为了解决这个问题，在特开平 7 - 206514 号公报上提出了这样一种氧化铝陶瓷，该氧化铝陶瓷含有 Al_2O_3 95 - 98 % (重量) 为主要成分，再添加由 SiO_2 40 - 85 % (重量)、 MgO 10 - 55 % (重量)、 CaO 5 - 50 % (重量) 组成的烧结助剂 2 - 5 % (重量)；此外，在特开平 7 - 237961 号公报上提出了一种以 Al_2O_3 达 90 - 95 % (重量) 为主要成分，再添加 SiO_2 3.0 - 5.0 % (重量)、 MgO 1.0 - 1.5 % (重量) 及 B_2O_3 0.5 - 3.5 % (重量) 所形成的氧化铝陶瓷。

25 在特开平 7 - 206514 号公报上提出的氧化铝陶瓷存在的问题是：该氧化铝陶瓷可由减少烧结助剂的添加量提高其耐磨性能；但是，由于其中氧化铝的含量越大，其烧结性能越低，因此，必须在高温下进行焙烧，而且，在该焙烧温度下的结晶的粒度分布易变宽，容易导致耐磨性的降低。另外，在将该氧化铝陶瓷用于粉碎用磨球时，可以看到，其空磨的磨耗，即，在球磨机中仅放入粉碎用磨球和水，使之旋转时的耐磨性显示出优异的性能。然而，在对如氧化铝等的粉体进行粉碎时的实际磨耗中，其耐磨性能尚未能充分满足。

30 又，在特开平 7 - 237961 号公报上提出的氧化铝陶瓷显示了与含有 Al_2O_3

达 90—95% (重量) 的以往的氧化铝陶瓷相同程度的优异的耐磨性，但其缺陷是：为抑制晶粒长大及降低焙烧温度而添加的 B_2O_3 在 1000℃ 下仍显示了相当的蒸汽压；由于在焙烧中易蒸发，所述的氧化铝陶瓷的组份易发生变动，这样，必然使其特性不稳定；另外，由于 B_2O_3 的蒸发，在陶瓷内部产生孔洞，导致耐磨性能低下。

因此，本发明的目的是，提供一种低成本的具有优异耐磨性能的氧化铝陶瓷，所述的氧化铝陶瓷可在低温下烧结，且其特性不稳定性小。

解决课题的手段

本发明为达到上述目的的手段是：提供一种耐磨性氧化铝陶瓷，所述氧化铝陶瓷由 Al_2O_3 88% (重量) 以上，95% (重量) 以下、辅助成分 5—12% (重量) 及杂质 0.5% (重量) 以下组成；所述辅助成分由 SiO_2 72—85% (重量)、 MgO 3—25% (重量)、 CaO 3—25% (重量) 组成；所述辅助成分中的各个成分对所述陶瓷整体所占重量百分比分别为 SiO_2 3.6—10% (重量)， MgO 0.2—2.5% (重量)， CaO 0.2—2.5% (重量)，所述陶瓷缺陷率在 5% 以下。

在本发明的说明书中，陶瓷的缺陷率是指：使用平面磨床按下列条件对陶瓷进行粗磨(削)加工之后，再作研磨加工，抛光成镜面，将经过镜面抛光的陶瓷面(以下称为镜面抛光面)在具有所定的放大倍率(通常为 500 倍)的扫描电子显微镜下作图像摄影，图像分析该摄影图像，由二元化将该摄影图像分离为缺陷部分和非缺陷部分，该缺陷部分占整个图像的面积的比例(即，面积比率)即指缺陷率。所述缺陷部分的缺陷不仅包含气孔，也包括在作烧结体的粗磨及研磨、抛光加工时发生脱粒后、及不对烧结体的体积密度值产生影响的水平面的缺陷。

上述的镜面抛光使用平面磨床和树脂结合剂型的金刚石砂轮按下列进行。首先，在 140 号粒度的金刚石砂轮上，取砂轮的周向速度为 1500 米/秒，切入深度为 $8 \mu m$ ，非磨削物的陶瓷(以下称为工件)的左右送给速度(以下称为工件送给)为 17 米/秒，磨削约 $80 \mu m$ 之后停止切入，来回转动 5 次。接着，换用 400 号粒度的金刚石砂轮，在砂轮的周向速度为 1500 米/秒，切入深度为 $5 \mu m$ ，工件送给为 13 米/秒的条件下，磨削约 $50 \mu m$ 之后停止切入，来回转动砂轮 10 次。再换用 600 号粒度的金刚石砂轮，在砂轮的周向速度为 1500 米/秒，切入深度为 $2 \mu m$ ，工件送给为 10/秒的条件下，磨削约 $20—30 \mu m$ 之后停止切入，来回转动砂轮 15 次。其后，以 $2.6 kgf/cm^2$ 压力将嵌埋有 $40 \mu m$ 的金刚石磨粒的金刚石带加压于已作磨削加工的陶瓷的磨削表面，作 3 分钟的研磨；再以 $2.6 kgf/cm^2$ 压力将嵌埋有 $6 \mu m$ 的金刚石磨粒的金刚石带加压，作 5 分钟的研磨；再以 $2.6 kgf/cm^2$ 压力将嵌埋有 $3 \mu m$ 的金刚石磨粒的金刚石

带加压，作 15 分钟的研磨；最后，以 1.3kgf/cm^2 压力将嵌埋有 $1 \mu \text{m}$ 的金刚石磨粒的金刚石带加压，作 5 分钟的研磨。

即，本发明的耐磨性氧化铝陶瓷的特征在于：所述的氧化铝陶瓷由 Al_2O_3 88 % (重量)以上、95 % (重量)以下、 SiO_2 3.6 - 10 % (重量)、 MgO 0.2 - 2.5 % (重量)、 CaO 0.2 - 2.5 % (重量)，残量实质上为无法避免的杂质组成；上述 SiO_2 、 MgO 及 CaO 的含量之和为 5 - 12 % (重量)；设上述 SiO_2 、 MgO 及 CaO 的含量之和为 100 计，则各成分的比例分别为 SiO_2 72 - 85 % (重量)、 MgO 3 - 25 % (重量)、 CaO 3 - 25 % (重量)，上述不可避免的杂质含量在 0.5 % (重量)以下，缺陷率在 5 % 以下。

作为上述主要成分的 Al_2O_3 的含量以 90 - 94.5 % (重量)的范围更好。又，作为上述辅助成分的含量以 SiO_2 5 - 10 % (重量)、 MgO 0.4 - 1.5 % (重量)、 CaO 0.3 - 1.5 % (重量)为好；上述各成分之和设为 100 时，各成分的比例分别为 SiO_2 73 - 84 % (重量)、 MgO 3.5 - 1 % (重量)、 CaO 4 - 15 % (重量)的范围为更佳。

另外，在本发明中，为了在进一步提高上述氧化铝陶瓷的强度及韧性的同时，使其细微组织更加均一，对每 100 重量份由上述成分组成的基本组合物添加 ZrO_2 0.01-15 重量份，较好的是 0.05-10 重量份，更好的是 0.1-8 重量份。

另外，本发明提供了一种耐磨性氧化铝陶瓷的制造方法，其特征在于，以所定的比例配合原料粉末，将该混合物作微粉碎至平均粒径为 0.5-1.0 μm 的粉末后，将所得的微粉末(模压)定形成所需的形状，得到体积密度为 1.90-2.10 g/cm^3 的成型体，焙烧该成型体。此时，粉碎后的微粉末的比表面积以 8 - 15 m^2/g 为宜，又，成型体的焙烧温度以 1350 - 1600 °C 为佳。

上述不可避免的杂质的含量设为 0.5% (重量)以下，但是，其中最好是将 Na_2O 及 K_2O 等的碱金属氧化物的含量设为 0.45% (重量)以下，较好的是 0.4% (重量)以下；又， TiO_2 的含量设为 0.2% (重量)以下，较好的是在 0.15% (重量)以下。

另外，所述的缺陷率对陶瓷的耐磨性能产生很大的影响，因此，镜面抛光面上的缺陷率最好控制在 5 % 以下。这是因为，缺陷比例超过 5 %，则这些缺陷即成为磨耗的起点，加快磨耗，导致耐磨性能的下降，同时，也导致抗冲击强度的低下，故不理想。较好的缺陷率为 3 % 以下，更理想的是在 2 % 以下。

发明的实施形态

如前所述，本发明的耐磨性氧化铝陶瓷是按如前所述的比例配合原料，粉碎混合物至其平均粒径在 1.0 μm 以下、其比表面积在 8 m^2/g 以上，更具体地，配制其平均粒径在 0.5-1.0 μm 、其比表面积在 8-15 m^2/g 的原料粉末，烧结成型所得的原料粉末至所定的形状，得到体积密度为 1.90-2.10 g/cm^3 的成型体，

在 1350 - 1600 °C 的温度下焙烧该成型体而加以制得的。具体的制造方法如下。

(1)首先，按上述的组份比将构成氧化铝陶瓷的各组成元素的化合物进行配制，必要时添加 ZrO_2 原料，在水或有机溶剂中，采用湿法，使用如球磨机、碾磨机等的已知的粉碎机进行粉碎、混合、分散，配制原料粉末。

作为主要成分的氧化铝原料，其纯度为 99.7% (重量)，比表面积为 $2m^2/g$ 以上，平均粒径在 $3.0 \mu m$ 以下，较好的是平均粒径在 $0.5 - 3.0 \mu m$ 。另外，该氧化铝原料可由明矾法等制得，但最好是使用拜耳法制得的氧化铝原料，该原料可廉价地制得。

作为辅助成分中的 MgO 及 CaO 的原料，可使用氧化物、氢氧化物、碳酸盐等的盐类，但最好是使用其平均粒径在 $3.0 \mu m$ 以下，较好的是平均粒径在 $0.5 - 3.0 \mu m$ 的盐类。又，作为 SiO_2 原料，可以使用硅石、石英、硅溶胶、硅酸四乙酯等，也可使用将 Y_2O_3 等的稀土类元素作为稳定剂固溶于如高岭土等的粘土矿物或 ZrO_2 中的正方晶系锆。作为该 ZrO_2 的原料，使用其平均粒径为 $1.0 \mu m$ 以下，较好的是使用其平均粒径在 $0.5 - 1.0 \mu m$ 的、其比表面积在 $5m^2/g$ 以上、较好的是在 $5 - 16m^2/g$ 以上的原料。在使用固溶有 Y_2O_3 等的稳定剂的正方晶系锆作为原料时，可由应力诱导相变效果而提高其韧性。

在上述氧化铝陶瓷的原料中，通常含有不可避免的杂质，例如， Fe_2O_3 、 Na_2O 、 K_2O 及 TiO_2 等，但是，由于不可避免的杂质中碱金属氧化物及 TiO_2 或是生成次生相，或是导致异常粒子的形成，所以，应使用其不可避免的杂质含量尽可能少的原料，特别是，由于 Na_2O 和 K_2O 容易和 SiO_2 等形成玻璃相，应选用碱金属氧化物的含量在 0.45% (重量) 以下的原料。又，由于 TiO_2 或是促进结晶成长，或是成为异常晶粒长大的原因，所以，应选择其含量为 0.2% (重量) 以下，更好的是选择 0.15% (重量) 以下的原料。

粉碎、混合及分散在水或有机溶剂中以湿法进行，这时，泥浆的粘性以 50 - 1500cps 为佳。粘性高时，最好适当添加如丙烯酸钠、多羧酸盐等的分散剂，调配粘性。由粉碎所得的粉体的平均粒径在 $1.0 \mu m$ 以下，比表面积在 $5m^2/g$ 以上，更具体的是将粉体粉碎至其平均粒径在 $0.5 - 1.0 \mu m$ ，其比表面积在 $8 - 15m^2/g$ 以上。欲进行这样粒度的粉碎，可使用如球磨机，用 20mm 直径的氧化铝制磨球粉碎 96 个小时而进行。

(2)对如上所得的泥浆干燥和造粒，得到造粒的粉末。干燥方法可根据所使用的成型方法而选用。通常，在使用模压或 CIP(各向同性冷轧压)法成型时，采用喷雾干燥；又在浇铸成型及转动造粒成型的场合或采用挤压成型及注射成型的场合，最好选用干燥器干燥。

重要的是，造粒的粉体即使在其后续工序的成型中的低压力下也能压碎，压碎性差的造粒粉体与烧结体所含的缺陷量的增加有关。压碎性良好的造粒粉

体可由适当选择添加于泥浆的粘合剂的种类、量及喷雾干燥器处理时的各种条件而得到。另外，作为粘合剂可使用如聚乙烯醇(PVA)、丙烯酸树脂、石蜡乳剂等以往所使用的任一种粘合剂；另外，作为分散剂，以使用丙烯酸钠、多羧酸盐等为好。

5 例如，在使用喷雾干燥器干燥的场合，对在前述工序中粉碎了的泥浆，可将对其固体成分(原料粉末)为1 - 5 % (重量)的粘合剂添加其中。在添加粘合剂时，当该粘合剂的粘性达500cps以上时，可添加分散剂将其粘性调节至500cps以下。所得的泥浆用喷雾干燥器在150 - 250℃的温度下喷雾干燥，造粒。该成型用的粉体通常配制成含水率为0.2-2%，粒径为40 - 100 μm的范围。其次，使用该粉体，根据制造陶瓷通常所用的方法，由模压、CIP等的方法，在500 - 20000kgf/cm²的成型压力下制得设定的形状。

10 又，在由转动造粒、浇铸成型、挤压成型、注射成型等的成型方法成型时，也可省略喷雾干燥工序，直接用泥浆，或仅仅用干燥成型用的原料粉体。例如，在使用浇铸成型法作为成型方法时，使用丙烯酸钠、聚羧酸盐等的分散剂，将粉碎了的泥浆的粘度调制成150cps以下，用石膏模成型。

15 在使用转动造粒成型作为成型方法时，将粘合剂加入粉碎的泥浆中，由干燥器在80 - 120℃下干燥，在雾化器之类的粉碎机中加以粉碎干燥粉体，通过40 - 80目网眼的筛子，得到筛下的粉体，该粉体直接用于转动造粒成型。

20 在使用挤压成型或注射成型作为成型方法时，在干燥器中，80 - 120℃下干燥粉碎的泥浆，在雾化器之类的粉碎机中粉碎干燥粉体，通过40 - 80目网眼的筛子，得到筛下的粉体，于此粉体中，在挤压成型的场合加入3 - 10%的粘合剂用混和机进行混合，在注射成型的场合，加入15 - 30%的粘合剂用混和机进行混合，调制成成型用的坯土，进行挤压成型或注射成型。

25 尽管如上所述的成型方法各有不同，但是，所得的成型体的体积密度都须在1.90g/cm³以上，更好的是在1.95g/cm³以上。当所得的成型体的体积密度不到1.90g/cm³时，则所得的烧结体中的缺陷增加，因此不理想。

在1350 - 1600℃，更好的是在1400 - 1550℃的温度下焙烧如上所得到的成型体，由此得到目的产品的耐磨性氧化铝陶瓷。

30 本发明有关的耐磨性氧化铝陶瓷的组份限于如上所述的范围内的理由如下。即，Al₂O₃的含量应为88% (重量)以上、95% (重量)以下，当Al₂O₃的含量不到88% (重量)时，则在烧结体内部生成的玻璃相及次生相的量增多，导致烧结体的强度、硬度低下，且其抗冲击性及耐磨性能也降低，因而不理想；又，当Al₂O₃的含量在95% (重量)以上时，则不仅在烧结体内部生成的玻璃相过少，导致烧结性能低下，且伴随着焙烧温度的上升，在氧化铝的晶界上易生成玻璃相的偏析，成为异常晶粒长大的原因，使其硬度、韧性及强度低下，因而也不理想。

又，作为上述辅助成分的 SiO_2 、 MgO 及 CaO 是作为烧结助剂添加的，这些辅助成分主要以玻璃相存在于氧化铝晶界上，抑制了其晶粒的成长，提高了体积密度和抑制了内部缺陷率，提高了耐磨性能。将各个辅助成分的含量限于上述范围之内是基于如下所述的理由。

即， SiO_2 、 MgO 及 CaO 的含量分别为 SiO_2 3.6 - 10% (重量)、 MgO 0.2 - 2.5% (重量)、 CaO 0.2 - 2.5% (重量) 的范围时，则不仅它们与 Al_2O_3 结晶的热膨胀差及润湿性能适当，晶体粒径及分布的控制容易，而且，氧化铝晶界强度及韧性提高，抗冲击性及耐磨性提高。然而，当 SiO_2 、 MgO 及 CaO 的三者中之一的含量超出上述范围，则除了氧化铝晶界强度降低，生成次生相粒子，及因与其它材料的冲击和摩擦导致结晶粒径的脱落、韧性低下之外，还有晶体在焙烧阶段变大，易发生异常晶粒的(过度)长大，必然地导致晶体粒径缺乏均一性，使抗冲击性及耐磨性下降，所以取上述的范围。

具体地，当 SiO_2 的含量不到 3.6% (重量) 时，氧化铝陶瓷的烧结性低下；又，当 SiO_2 的含量超过 10% (重量) 时，引起氧化铝陶瓷的晶界强度低下，故取上述之值。另外，当 MgO 的含量不到 0.2% (重量) 时，氧化铝陶瓷的晶体粒径缺乏均一性；当 MgO 的含量大于 2.5% (重量) 时，则析出次生相，所以取 MgO 的含量为 0.2 - 2.5% (重量)。再有，当 CaO 的含量不到 0.2% (重量) 时，氧化铝陶瓷的烧结性低下；而当其含量超过 2.5% (重量) 时，则又导致氧化铝陶瓷的烧结性的低下和异常晶粒的成长，因此取 CaO 的含量为 0.2 - 2.5% (重量)。

另外， SiO_2 、 MgO 及 CaO 的含量之和，即，辅助成分的含量取为 5 - 12% (重量)，这是因为：当上述成分含量之和不到 5% (重量) 时，存在于氧化铝晶界的玻璃相的量减少使玻璃相的存在不均匀，产生烧结性的下降和晶体的异常晶粒的长大，导致氧化铝陶瓷的抗冲击性及耐磨性能的低下，所以，不宜使用。另一方面，当辅助成分的含量超过 12% (重量)，则玻璃相生成过多，导致氧化铝陶瓷的硬度、韧性及强度低下，降低氧化铝陶瓷的抗冲击性及耐磨性能，所以取上述范围。

再有，设定上述 SiO_2 、 MgO 及 CaO 的含量之和为 100 时，各成分的比例分别为 SiO_2 72 - 85% (重量)、 MgO 3 - 25% (重量)、 CaO 3 - 25% (重量) 的理由如下。即，当辅助成分中 SiO_2 的含量不到 72% (重量) 时，氧化铝陶瓷的烧结性低下；又，当辅助成分中 SiO_2 的含量超过 85% (重量) 时，玻璃相的量增加，所以取上述范围。另外，当 MgO 的含量不到 3% (重量) 时，氧化铝陶瓷的晶体粒径缺乏均一性；当 MgO 的含量超过 25% (重量) 时，则析出次生相，所以取 MgO 在辅助成分中的含量为 上述范围。再有，当辅助成分中 CaO 的含量不到 3% (重量) 时，氧化铝陶瓷的烧结性低下；而当其含量超过 25% (重量) 时，则不光导致氧化铝陶瓷的烧结性的低下，且易使晶体成长，所以，取

其含量为上述范围。

本发明的耐磨性氧化铝陶瓷针对 100 重量份的上述成分组成的基本组合物添加 0.01-15 重量份的 ZrO_2 ，由此，可进一步提高强度和韧性，同时，使氧化铝晶界的玻璃相作均一的分散；而且，也可缩小晶体粒径的分布，使烧结体的组织均匀。该 ZrO_2 的添加量取为上述范围是因为：当其添加量对每 100 重量份由上述成分组成的基本组合物不到 0.01 重量份时，则不能得到充分的效果，如果该添加量超过 15 重量份，则又导致硬度的低下，特别是，在使用未添加稳定剂的 ZrO_2 粉体时，烧结体中易存在单斜晶系锆，会发生微裂纹，使其耐磨性能和抗冲击性低下，因此，不理想。上述 ZrO_2 的添加量以对于每 100 重量份的上述基本组份为 0.01-15 重量份，较好的是 0.05-10 重量份，更好的是 0.1-3 重量份。

此时，添加的 ZrO_2 原料最好使用其平均粒径在 $1.0 \mu m$ 以下的原料。这是因为，当 ZrO_2 原料的平均粒径超过 $1.0 \mu m$ ，则烧结体中易存在单斜晶系锆，会发生微裂纹，使其耐磨性能和抗冲击性低下，因此，不理想。又，作为 ZrO_2 原料也可使用固溶有稀土类元素氧化物等的稳定剂的原料。此时，含有稀土类元素氧化物，例如，含有 Y_2O_3 为稳定剂的 ZrO_2 原料，最好是使用 Y_2O_3 的含量在 5 % (摩尔) 以下的原料，由此，可由锆的应力诱导相变效果而提高韧性。

如前所述，根据本发明，以设定的比例对于主成分的 Al_2O_3 添加特定量的特定辅助成分，同时，抑制原料中所含有的不可避免的杂质的量，由此，可得到具有优异的耐磨性的氧化铝陶瓷，上述氧化铝陶瓷具有 $1.0-5.0 \mu m$ 的范围内的平均晶体粒径和， $3.60g/cm^3$ 以上的体积密度，且由气孔和磨光加工引起的脱粒等的缺陷较少，为 5 % 以下。

另外，当烧结体的平均晶体粒径超过 $5 \mu m$ 时，则引起氧化铝陶瓷的硬度低下，耐磨性能降低，故不理想。该烧结体的平均晶体粒径最好在 $3 \mu m$ 以下，更好的是在 $2.5 \mu m$ 以下。又，在耐削性能不成问题的场合，考虑到其与耐磨性能的平衡，最好设定在 $5 \mu m$ 以下的范围。再有，当其最大粒径(累积容积为 100 % 时的晶体粒径)超过 $10 \mu m$ 时，则晶体粒径分布变宽，硬度低下。其结果与耐磨性能的低下有关，不宜采用，故最好是使用最大粒径在 $10 \mu m$ 以下，更好的是 $8 \mu m$ 以下的烧结体。

又，体积密度取为 $3.60g/cm^3$ 以上，这是因为，当体积密度不到 $3.60g/cm^3$ ，则烧结度不够，同时，存在很多成为缺陷的孔洞，这不光引起强度、硬度及韧性的低下，且加速磨损，因此不理想。体积密度取 $3.65g/cm^3$ 以上为宜。

本发明的氧化铝陶瓷由于晶体粒径小，晶体致密，缺陷少而具有优异的抗冲击性和耐磨性能。因此，比起以往的、 Al_2O_3 含量相同水准的烧结体来，本发明的氧化铝陶瓷强度高、硬度大，韧性好。本发明的氧化铝陶瓷的威氏硬度

显示了负荷 10kgf 下的 1100 以上的高硬度，又，其弯曲强度显示了 JIS1601 规定的 3 点弯曲法下的 $40\text{kgf}/\text{mm}^2$ 以上的高强度。再有，本发明的氧化铝陶瓷在作成如粉碎用的磨球那样的球状时，将一个磨球体嵌于超硬合金板上，施加应力，测得抗压强度为 $25\text{kgf}/\text{mm}^2$ 以上。该抗压强度(σ_c)可从式： $\sigma_c = 4 \times P / (\pi \times D^2) (\text{kgf}/\text{mm}^2)$ 得到。式中， P 为破坏强度(kgf)， D 为球体直径(mm)。

威氏硬度在不到 1100 时，使其耐磨性能下降，所以不理想。又弯曲强度不到 $40\text{kgf}/\text{mm}^2$ 或抗压强度不到 $25\text{kgf}/\text{mm}^2$ 时，会影响到降低抗冲击性和耐磨性能，也不理想。再有，破坏韧性在按 JIS1607(IF 法)规定的测试方法中为 $3.0\text{MPa} \cdot \sqrt{\text{m}}$ 以上。

实施例 1

将各原料按表 1、表 2 的组成进行掺合，得到烧结体，所得的各混合物用 92 % 的氧化铝制球磨机(容量 7.2 立升)和 20mm 直径的 92 % 氧化铝制粉碎球在浓度 60 % 下作湿式粉碎 48 小时，得到含有如表 3、表 4 所示的平均粒径、比表面积在 $8\text{m}^2/\text{g}$ 以上的微粉末的泥浆。对所得的泥浆加入聚乙烯醇水溶液 3 - 5 % (重量)，作为粘合剂，调节粘度为 350cps，用维持在 200 °C 的喷雾干燥器干燥，造粒，得到成型用粉体。在成型压力为 1ton f/cm^2 (仅在 20 号及 38 号试样的成型压力为 $300\text{kgf}/\text{cm}^2$)，由 CIP 成型法将该成型用粉体成型为球状及板状。所得的成型体在 1380 - 1600 °C 下焙烧，得到直径 10mm 的球体及 $50 \times 50 \times 4\text{mm}$ 的板。球体经转筒抛光后，用作粉碎用球，板则经切断及磨削加工后用作 JIS1601 规定的弯曲强度测试用的试片。

作为氧化铝材料，关于 1 - 21、24 - 39 号试样，是分别使用了根据拜耳法制得的凝聚的二次粒径为 $45 \mu\text{m}$ 、比表面积为 $2.5\text{m}^2/\text{g}$ 的纯度为 99.6 % 的低钠氧化铝原料。关于 22 号试样，是使用了平均粒径为 $1.0 \mu\text{m}$ 、比表面积为 $6\text{m}^2/\text{g}$ 的纯度为 99.8 % 的活性氧化铝原料。关于 23 号试样，是使用了根据拜耳法制得的凝聚的二次粒径为 $55 \mu\text{m}$ 、比表面积为 $1.5\text{m}^2/\text{g}$ 的纯度为 99.7 % 的低钠氧化铝原料。

另外，作为 MgO 及 CaO 的原料，使用纯度为 99.5 % 的碳酸盐，作为 SiO_2 的原料使用高岭土。作为 ZrO_2 的原料，在 5、8、10、15 及 25 号试样中使用了其平均粒径在 $1.0 \mu\text{m}$ ；其比表面积在 $12\text{m}^2/\text{g}$ 、纯度为 99.9 % 的二氧化锆，在 13 号试样中，使用了含有 $\text{Y}_2\text{O}_3 2.8\%$ (摩尔)、平均粒径在 $0.5 \mu\text{m}$ ，其比表面积为 $18\text{m}^2/\text{g}$ 的二氧化锆。

使用得到的各个粉碎用的球，按如下所述的方法进行耐磨性试验。即，将粉碎用的球装入 2 升容量的氧化铝制(纯度 92 %)的球磨机中，至该球磨机的容积的一半，放入平均粒径 $25 \mu\text{m}$ 、比表面积为 $1.2\text{m}^2/\text{g}$ 的氧化铝原料粉体 900g 和水 0.7 升，在球磨机旋转速度为 100rpm 下粉碎 24 小时。从测试前后的

球的重量差求出相对于测试前的球重量的百分率，将其作为磨耗率。所得的结果与粉碎用的球的体积密度、晶体粒径、缺陷量、威氏硬度及弯曲强度，及成型体的体积密度、粉碎粉体的平均粒径及比表面积一起示于表 3、表 4。弯曲强度用由板加工而成的测试片测定。

表 1

试样 No.	主成分 Al_2O_3 (重量%)	基本组合物						杂质 (重量%)			ZrO_2 添加量 (重量份)
		副成分(重量%)			副成分组成			$\text{Na}_2\text{O} + \text{K}_2\text{O}$	TiO_2	其它	
		SiO_2	MgO	CaO	SiO_2	MgO	CaO	$\text{Na}_2\text{O} + \text{K}_2\text{O}$	TiO_2	其它	总量(%)
1	92.69	6.84	5.04	0.40	1.40	73.6	5.9	20.5	0.35	0.07	0.05
2	91.73	7.85	6.04	0.67	1.14	77.0	8.5	14.5	0.32	0.06	0.04
3	93.06	6.51	5.38	0.77	0.36	82.7	11.8	5.5	0.30	0.07	0.06
4	91.54	8.00	6.64	1.00	0.36	83.0	12.5	4.5	0.34	0.06	0.06
5	92.69	6.84	5.04	0.40	1.40	73.6	5.9	20.5	0.35	0.07	0.05
6	89.71	9.85	7.12	2.38	0.35	72.2	24.2	3.6	0.33	0.06	0.05
7	92.55	7.00	5.92	0.25	0.83	84.5	3.6	11.9	0.34	0.06	0.05
8	91.34	8.20	6.89	0.73	0.58	84.0	8.9	7.1	0.34	0.05	0.07
9	93.16	6.35	4.83	0.92	0.60	76.1	14.5	9.4	0.33	0.09	0.07
10	93.73	5.80	4.61	0.70	0.49	79.4	12.1	8.5	0.33	0.08	0.06
11	88.97	10.54	7.70	0.41	2.43	73.1	3.9	23.1	0.32	0.10	0.07
12	92.38	7.18	5.38	1.48	0.32	74.9	20.6	4.5	0.31	0.07	0.06
13	94.30	5.21	4.11	0.67	0.43	78.8	12.9	8.3	0.36	0.09	0.04
14	90.58	8.95	6.46	1.49	1.00	72.2	16.7	11.1	0.35	0.07	0.05
15	93.04	6.50	5.36	0.79	0.35	82.4	12.2	5.4	0.33	0.06	0.07
16	90.28	9.25	7.32	0.88	1.05	79.2	9.5	11.3	0.34	0.05	0.08
17	88.02	11.50	8.66	1.41	1.43	75.3	12.3	12.4	0.38	0.05	0.07
18	92.25	7.26	5.13	1.41	0.72	70.6	19.5	9.9	0.36	0.05	0.08

表 2 (续表 1)

	94.98	4.58	3.30	0.64	0.64	72.0	14.0	14.0	0.31	0.08	0.05	0.44	0
19	92.30	7.27	5.89	0.32	1.06	81.0	4.4	14.6	0.32	0.05	0.06	0.43	0
20	90.44	9.09	7.50	1.39	0.20	82.5	15.3	2.2	0.35	0.06	0.06	0.47	0
21	96.51	3.00	2.53	0.30	0.17	84.3	10.0	5.7	0.35	0.09	0.05	0.49	0
22	91.56	7.98	6.40	0.83	0.75	80.2	10.4	9.4	0.32	0.07	0.07	0.46	0
23	93.32	5.14	4.33	0.18	0.63	84.3	3.5	12.2	0.31	0.07	0.05	0.43	0
24	90.28	9.25	7.32	0.88	1.05	79.2	9.5	11.3	0.34	0.05	0.08	0.47	16.0
25	88.07	11.43	9.2	0.24	1.99	80.5	2.1	17.4	0.37	0.06	0.07	0.50	0
26	90.07	9.49	6.69	0.36	2.44	70.5	3.8	25.7	0.31	0.07	0.06	0.44	0
27	87.60	11.97	9.80	0.90	1.27	81.9	7.5	10.6	0.32	0.05	0.06	0.43	0
28	92.39	6.63	4.98	0.43	1.22	75.1	6.5	18.4	0.33	0.58	0.07	0.98	0
29	88.82	10.73	7.74	0.36	2.63	72.1	3.4	24.5	0.33	0.05	0.07	0.45	0
30	93.57	6.00	5.00	0.81	0.19	83.4	13.5	3.1	0.30	0.06	0.07	0.43	0
31	90.00	9.57	6.80	2.45	0.32	71.1	25.6	3.3	0.31	0.06	0.06	0.43	0
32	90.77	8.76	7.64	0.83	0.29	87.2	9.5	3.3	0.30	0.10	0.07	0.47	0
33	91.54	7.76	6.57	0.83	0.36	84.7	10.7	4.6	0.55	0.07	0.08	0.70	0
34	88.91	10.66	7.70	2.59	0.37	72.2	24.3	3.5	0.32	0.06	0.05	0.43	0
35	87.14	12.37	10.50	0.73	1.14	84.9	5.9	9.2	0.34	0.08	0.06	0.49	0
36	91.89	7.51	6.29	0.47	0.75	83.8	6.2	10.0	0.32	0.07	0.21	0.60	0
37	91.50	8.05	6.08	0.57	1.40	75.5	7.1	17.4	0.34	0.06	0.05	0.45	0
38	92.59	6.95	5.85	0.35	0.75	84.2	5.0	10.8	0.35	0.07	0.04	0.46	0

表 3

试样 No.	平均粒径 (μm)	成形体 体积密度 (g/cm ³)	焙烧温度 (℃)	体积密度 (g/cm ³)	晶体质粒径 (μm)		缺口量 (%)	HV	弯曲强度 (kgF/mm ²)	磨损率 (%)
					平均值	最大值				
1	0.75	2.00	1520	3.70	2.3	4.8	0.9	1210	43	0.08
2	0.81	2.02	1470	3.68	1.8	4.2	0.9	1200	44	0.05
3	0.75	2.04	1450	3.69	1.2	2.8	0.5	1250	42	0.04
4	0.90	2.10	1500	3.72	2.0	4.0	0.7	1210	41	0.05
5	0.88	2.07	1450	3.79	1.3	2.5	0.6	1190	52	0.02
6	0.76	2.06	1550	3.65	2.8	4.2	2.2	1180	41	0.09
7	0.85	2.09	1460	3.68	1.7	4.3	1.2	1210	46	0.06
8	0.89	1.99	1380	3.73	1.2	2.5	1.0	1220	46	0.03
9	0.75	2.03	1480	3.72	1.7	3.5	0.9	1210	45	0.05
10	0.73	1.98	1470	3.72	1.9	3.7	0.6	1220	42	0.04
11	0.77	2.02	1450	3.68	1.7	3.9	2.3	1180	40	0.09
12	0.95	2.00	1500	3.70	2.1	3.9	2.9	1200	40	0.07
13	0.70	2.04	1400	3.73	1.5	2.3	0.9	1190	48	0.02
14	0.85	1.99	1500	3.70	1.9	3.8	1.5	1200	43	0.07
15	0.87	2.03	1430	3.72	1.2	3.0	0.7	1200	44	0.03
16	0.87	2.01	1490	3.70	2.1	4.2	1.7	1180	42	0.05
17	0.92	2.01	1430	3.60	1.3	3.0	3.9	1130	40	0.08
18	0.91	2.02	1480	3.65	2.2	4.8	7.2	1010	37	0.71

表4(续表3)

	1.9	0.78	2.00	1530	3.70	2.4	7.5	6.0	1100	37	0.52
20	0.70	1.75	1500	3.57	2.8	5.8	9.8	1080	32	0.75	
21	0.78	2.00	1460	3.65	2.7	5.2	6.0	1020	37	0.49	
22	0.80	1.92	1520	3.78	2.3	3.5	9.6	1350	45	0.21	
23	1.25	1.94	1470	3.53	1.1	3.2	12.0	980	35	3.1	
24	0.92	1.98	1480	3.68	2.2	7.8	8.5	1020	36	0.65	
25	0.76	2.04	1500	3.72	3.8	7.1	9.5	1040	32	1.7	
26	0.91	2.01	1500	3.67	2.8	7.0	6.8	1010	39	1.8	
27	0.75	2.00	1480	3.62	3.7	8.5	8.9	990	35	2.1	
28	0.81	2.09	1520	3.66	2.7	6.5	8.0	1000	38	1.0	
29	0.98	1.99	1530	3.67	4.0	10.5	6.2	1000	35	3.5	
30	0.95	1.93	1470	3.65	3.6	7.2	8.7	1100	34	1.9	
31	0.82	1.98	1480	3.64	2.5	5.9	5.7	1010	37	0.88	
32	0.88	2.02	1500	3.63	2.7	6.2	7.8	1000	34	0.90	
33	0.80	2.01	1470	3.67	2.3	5.6	6.3	1070	35	0.47	
34	0.77	2.01	1470	3.66	1.8	3.5	8.0	1130	39	0.95	
35	0.80	1.92	1520	3.66	3.0	7.0	9.6	1000	33	2.0	
36	0.95	1.93	1480	3.63	2.2	6.9	6.8	1010	36	1.3	
37	0.84	1.96	1550	3.65	4.5	9.0	7.8	1000	35	3.9	
38	0.75	1.82	1550	3.60	4.3	8.9	8.5	1100	36	3.7	
39	1.34	2.01	1580	3.62	5.2	9.5	7.9	1010	33	4.3	

在表 1、表 2 中, ZrO_2 的添加量以对于由氧化铝、烧结助剂及不可避免的杂质组成的基本组合物 100 重量份的添加量(重量份)表示。又, 在表 1、表 2 及表 3 和表 4 中, 试样 1 - 17 的烧结体是满足了本发明的条件的, 但试样 18 - 39 为至少没有满足本发明所规定的条件之一的、落于本发明的范围之外的烧结体。

平均晶体粒径是在金刚石砂轮上将烧结体按 140 号 - 400 号 - 600 号的顺序进行磨削加工之后, 再在金刚石砂轮上按 $40 \mu m - 6 \mu m - 3 \mu m - 1 \mu m$ 的顺序作研磨加工, 抛光成镜面。对此, 再作热蚀刻, 接着在扫描电子显微镜上以视野内可观察 100 个以上的晶体的放大倍率作观察, 然后照相摄影。由图像解析, 从该摄影照片测定一个晶体的面积, 换算为等价圆直径(D), 以 $D \times 1.5$ 为其晶体粒径, 如此, 测得 100 个晶体的晶体粒径。根据该值算出晶体的容积, 以累积容积为 50 % 时的晶体粒径为平均晶体粒径。

另外, 烧结体的缺陷量如下求得。将供作测试的试样如同晶体粒径的测试时一样, 进行镜面抛光。该镜面抛光的面直接在扫描电子显微镜下以 500 的比率进行观察, 照相摄影, 其照片由图像解析二元化, 分为缺陷部分和非缺陷部分。求得缺陷部分所占面积率(%), 将此作为烧结体的缺陷量。不光是气孔, 该缺陷也包括在对烧结体作如上所述的磨削及研磨抛光时所发生的脱粒后的缺陷, 及未对烧结体的密度产生影响的水准面的缺陷。本发明的氧化铝陶瓷(试样 1 号)及本发明的范围外的氧化铝陶瓷(试样 22 号)的镜面抛光后的面, 作扫描电子显微镜的照相摄影后, 由图像解析二元化分为缺陷部分和非缺陷部分的图示于图 1 及图 2。图中, 黑色部分表示缺陷。

从表 3、表 4 的结果可明白, 本发明的氧化铝陶瓷制的粉碎用的球, 显示了 0.1 以下的磨耗率和优秀的耐磨性能。另外, 从图 1 及 2 所示的结果可以明白, 本发明的氧化铝陶瓷的缺陷量极低, 仅为 0.5 %, 相比之下, 试样 22 号的缺陷量极高, 为 9.6 %。又, 从试样 38 及 39 号的结果可以明白, 其成分组成虽然落在本发明的范围内, 但其缺陷量若多, 则耐磨性能就低下, 而且, 该缺陷量受其制造过程中的粉碎后的平均粒径及成型体体积密度所左右。

从以上的说明可以明白, 根据本发明, 可以得到具有优异特性的耐磨性氧化铝陶瓷, 所述的氧化铝陶瓷由于 a) 因为具有优异的强度、硬度、韧性及抗冲击性, 其高负荷下的耐磨性能良好; b) 由于在用作粉碎机用的部件时具有优异的耐磨性能, 故极少有磨耗粉体混入被粉碎物中, 而且, 即使有微量磨耗粉末混入, 由于磨耗粉末极其细微, 很少会损坏被粉碎物的均匀性; c) 其原料可以使用廉价的氧化铝。

从而, 本发明的氧化铝陶瓷不光可用作粉碎、分散用的介质、粉碎机的内衬材料, 容器、搅拌器等的粉碎机用构件, 最适用于各种产业的耐磨构件。

附图的简单说明

图 1 所示为本发明的氧化铝陶瓷作镜面抛光面的二元化图像的说明图。

图 2 所示为在本发明范围外的氧化铝陶瓷作镜面抛光面的二元化图像的说明图。

说 明 书 附 图



图 1

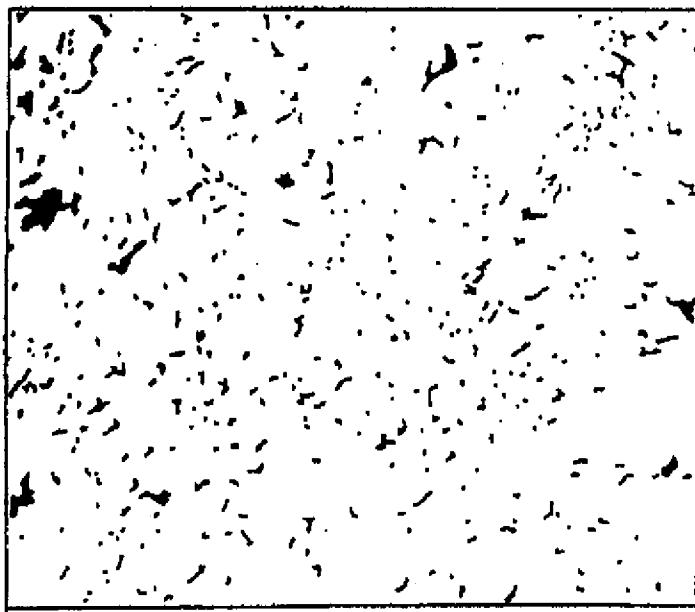


图 2